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**基于新型氨基硫醇单体的高选择性 Hg
(II) 印记聚合物的合成、表征和分析应用**

**Synthesis, Characterization and Analytical Application of a
High Selective Hg(II)-Imprinted Polymer Prepared from a
Novel Aminothiol Monomer**

Mahmoud Firouzzare

指导教师姓名: 王秋泉 教授

专 业 名 称: 分析化学

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High Selective Hg(II)-Imprinted Polymer Prepared from a
Novel Aminothiol Monomer**

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Mahmoud Firouzzare

Supervisor: Professor Qiuquan Wang

Department of Chemistry

College of Chemistry and Chemical Engineering

Xiamen University

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Abstract

Molecular imprinting is a technique for producing the special polymers which are able to adsorb a special molecule or ion selectively. These polymers create the recognition sites in a macromolecular matrix via imprinting by using a molecular or ionic template. The size and three dimensional image of template and alignment of the functional groups to interact with the target are memorized in the macromolecular matrix after removing the target molecule. The complexation, copolymerization and removing the template after polymerization are the main steps for preparation of ion imprinted polymers (IIPs). The right selection of functional monomer which has high affinity to the ion template is important and effects directly on selectivity.

Since the mercury shows very high affinity to sulfur, the functional monomers containing the sulfhydryl group can produce good stable complex with mercury.

The objective of this thesis is the preparation of a novel high selective Hg(II)-imprinted polymer from 2-Mercaptoethyl amine (MEA) and study on its characterization and analytical application. Since the planned ligand monomer for complexing the mercury ion was novel and not commercially available, it had to be first synthesized in the laboratory. MEA is the simplest stable aminothiols and has NH_2 and SH functional groups in its two ends, which was used for synthesis of a novel polymerizable ligand as called N-methacryloyl-2-mercapto ethylamine (MMEA) by methacryloylating the amino group. Then MMEA was used for complexing the Hg(II) ion via the formation Hg-S bonding. The synthesized complex monomer was applied for preparing a polymer by radical copolymerization with methacrylic acid (MAA) and ethylene glycol dimethacrylate (EDMA) and AIBN as the functional monomer, cross-linker and initiator respectively in the presence of a binary porogen of DMSO and toluene. An Hg(II)-imprinted polymer was obtained after removing the mercury ion from the prepared copolymer that presented a good adsorption capacity and selectivity for mercury in comparison with some competitor ions such as Cd(II) and Zn(II) and CH_3HgCl and with non-imprinted polymer. The Hg-imprinted polymer was also successfully applied for determination of Hg(II) ions in some complex matrices such as tap water and sea water samples.

Abstract

The structure of this thesis contains a general introduction on molecular imprinting and issues relevant to the research in chapter 1. Chapter 2 reports the experimental processes about the synthesis of N-methacryloyl-2-mercapto ethylamine monomer (MMEA) and then Hg(II)-N-methacryloyl-2-mercaptoethyl amine complex monomer (Hg(II)-MMEA) and also the preparation method of Hg(II)-imprinted copolymer. This chapter also contains the spectroscopic data of the synthesized materials and some discussion about the obtained results. The characterization results of the prepared Hg(II)-imprinted copolymer in related to adsorption capacity, pH and kinetics of adsorption and selectivity parameters are presented and discussed in chapter 3. Chapter 4 describes the analytical application of the prepared Hg(II)-imprinted copolymer in matrices of tap water and sea water samples. Chapter 5 describes the other experiments and studies performed in this thesis contain complexing the methylmercury, Preparation of SPME fibers and thermal stability of the prepared Hg(II)-Imprinted copolymer. Chapter 6 summarizes the conclusions from the thesis, as well as the comments for future perspectives. IR and RAMAN spectra are included in the appendix.

Keywords: Molecular Imprinting; Mercury Ion; 2-Mercaptoethyl Amine; N-methacryloyl-2-mercaptoethyl amine; Hg(II)-Imprinted Polymer; SPME; Thermal stability

厦门大学

Abstract in Chinese (摘要)

基于新型氨基硫醇单体的高选择性 Hg(II) 印记聚合物的合成、表征和分析应用

分子印迹是通过制备对特定目标分子或离子即模板分子（印迹分子）具有特异预定选择性的聚合物来选择性吸附/富集目标分子或离子的技术。此聚合物通过印迹模板分子或离子在分子基质中创造识别位点。除去模板分子后，模板分子的尺寸、立体结构和与模板分子相互作用的功能基团空间位置保留于分子基质中。络合、共聚和聚合后移除模板分子是制作离子印迹共聚物的主要步骤。正确选择对模板离子具有高亲和性的功能单体非常重要，直接影响其选择性。

由于汞表现出对硫具有非常高的亲和力，因此含巯基的功能单体与汞能够产生具有良好稳定性的复合物。

本论文的目的在于采用 2-巯基乙胺（MEA）合成对 Hg(II) 具有高亲合性的新印迹聚合物，并对其表征和分析应用的研究。新研究的与汞离子络合的配位单体无市售，第一次在本实验室合成。MEA 是最简单稳定的氨基硫醇化合物，功能基团 NH_2 和 SH 在其两端。MEA 通过氨基基团的甲基丙烯酸化合成新聚合物配体 N-甲基丙烯酰基-2-巯基乙胺(MMEA)。MMEA 通过形成 Hg-S 键用于络合 Hg(II)。合成的复杂单基体通过自由基共聚合作用合成聚合物，甲基丙烯酸(MAA)、乙二醇二甲基丙烯酸酯(EDMA)和 AIBN 在致孔剂 DMSO 和苯存在条件下分别作为功能单体、交联剂和引发剂。在从合成的共聚物中移除 Hg(II) 后所得的印迹聚合物对 Hg(II) 相比较其他的竞争离子如 Cd(II) 、 Zn(II) 、 CH_3HgCl 和非印迹的聚合物等展现了很好的吸附容量和选择性。Hg 印迹的聚合物也用于测定复杂基质如自来水和海水中的 Hg(II)。

第一章综述了关于分子印迹和与研究相关的一些问题。第二章报告了有关 N-甲基丙烯酰基-2-巯基乙胺单基体（MMEA）和 Hg(II)-N-甲基丙烯酰基-2-巯基乙胺复合单基体(Hg(II)-MMEA)的实验合成过程及 Hg(II)印迹聚合物的制作方法。此章也包括合成材料的光谱数据和对所得结果的讨论。第三章描述制得的 Hg(II)印迹共

摘要

聚物在吸附容量, pH 值和动力学吸附和选择性参数的特性, 并进行讨论。第四章对 Hg(II)印迹共聚物在自来水和海水基质中的应用进行了叙述。第五章论述了本课题中其他的一些实验研究包括络合甲基汞、制备固相微萃取纤维和制备热稳定的 Hg(II)印迹共聚物。第六章总结了本论文的研究工作, 并对将来进一步的研究工作进行了展望。红外光谱和拉曼光谱数据包含在附录中。

关键词

分子印迹; 汞离子; 2-巯基乙胺; N-甲基丙烯酰基-2-巯基乙胺; Hg(II)印迹聚合物; 固相微萃取

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Table of Contents

Abstract in English	I
Abstract in Chinese (摘要)	III
Acknowledgments	V
List of Figures	VIII
List of Tables	XI
Abbreviations	XII
Chapter 1 Introduction	1
1.1 Environmental Importance of Mercury	1
1.2 The Historical View to Molecular Imprinting	2
1.3 General Principle	4
1.4 Types of Interaction	6
1.4.1 Covalent Imprinting.....	6
1.4.2 Non-Covalent Imprinting.....	8
1.5 Advantages and Disadvantages of Covalent and Non-Covalent Imprinting	12
1.6 Metal Ion Imprinting	15
1.7 Polymer Synthesis	19
1.7.1 Free Radical Polymerization.....	19
1.7.2 Copolymerization and Cross-linking	22
1.7.3 Pore Formation Mechanism in MIPs.....	23
1.8 Optimization	24
1.8.1 Solvent.....	24
1.8.2 Temperature.....	25
1.8.3 Cross-linker and Monomer.....	26
1.8.4 Site Stability, Integrity and Accessibility.....	31
Chapter 2 Experimental Processes	33
2.1 Introduction	34
2.2 Adding the Polymerizable Groups and General Synthesis of Acryl Type Monomers	37
2.3 Materials and Instruments	39

Table of Contents

2.4 Synthesis of N-methacryloyl-2-mercapto Ethylamine Monomer (MMEA)	40
2.4.1 Experiment.....	40
2.4.2 Results and Discussion.....	41
2.4.3 Spectroscopic Data.....	43
2.5 Synthesis of Hg(II)–N-methacryloyl-2-mercapto Ethylamine Complex Monomer (Hg(II)-MMEA)	45
2.5.1 Experiment.....	45
2.5.2 Results and Discussion.....	46
2-5-3 Spectroscopic Data.....	48
2.6 Preparation of Hg(II)-imprinted and Non-imprinted Copolymers	49
2.6.1 Experiment.....	49
2.6.2 Results and Discussion.....	51
2.6.3 Spectroscopic Data.....	53
Chapter 3 Characterization	55
3.1 Introduction	55
3.2 Experiments	58
3.3 Results and Discussion	59
3.3.1 Adsorption Capacity of Imprinted Copolymer for Hg(II).....	59
3.3.2 Effect of pH on the Absorption behaviours.....	61
3.3-3 Kinetics of Adsorption.....	62
3.3-4 Selectivity.....	63
Chapter 4 Analytical Application	66
Chapter 5 The Other Experiments	67
5.1 Complexing the Methyl Mercury	67
5.2 Preparation of SPME Fibers	68
5-3 Thermal Stability of Prepared Hg(II)-Imprinted Copolymer	72
Chapter 6 Conclusion and Comments	74
References	76
Appendix (IR & Raman Spectra)	93

List of Figures

Figure 1.1 Schematic representation of the molecular imprinting principle.....	4
Figure 1.2 The covalent approach to molecular imprinting in organic polymers.....	6
Figure 1.3 Non-covalent imprinting by theophylline.....	9
Figure 1.4 Common functional monomers used in non-covalent molecular imprinting procedures.....	11
Figure 1.5 Interaction between metal ions and PVP.....	15
Figure 1.6 Metal ion-imprinted polymers from metal ion-coordinated vinyl monomers.....	16
Figure 1.7 Cu(II)-acrylic acid complex.....	17
Figure 1.8 Free radical addition polymerization of MAA using AIBN as initiator...20	
Figure 1.9 Free radical copolymerization of methyl methacrylate with <i>n</i> -butyl methacrylate.....	22
Figure 1.10 Schematic representation showing polymers with different topologies: linear, branched, macroscopic network and microgel.....	23
Figure 1.11 Schematic representation of the cross-linked polymer network arising from the copolymerisation of styrene with <i>p</i> -divinylbenzene.....	24
Figure 1.12 Schematic representation of the cross-linked polymer network arising from the copolymerization of methacrylic acid and ethylene glycol dimethacrylate..24	
Figure 1.13 Model of morphology formation that provides the porous network in MIPs.....	25
Figure 1.14 Some of common cross-linkers used in molecular imprinted polymers..28	
Figure 1.15 Polymer pseudo-phase diagram	30
Figure 1.16 Different types of binding sites in polymers containing micro- meso- and macro-pores.....	32
Figure 2.1 The repeated unit of Hg(II) imprinted copolymers complex with DAAB and VP.....	33
Figure 2.2 5,7-dichloroquinoline-8-ol.....	34
Figure 2.3 Some samples of aminothiols.....	35
Figure 2.4 The determined structure for Hg(Cys) ₂	36
Figure 2.5 Addition of an Acryl Fragment.....	38
Figure 2.6 Scheme of reaction system for synthesis of MMEA.....	40
Figure 2.7 Synthesis of MMEA.....	41
Figure 2.8 Schotten-Baumann reaction.....	41

List of Figures

Figure 2.9 Mechanism of Schotten-Baumann reaction.....	42
Figure 2.10 Mechanism of Synthesis of MMEA.....	42
Figure 2.11 The vibrations of amide II in secondary amides.....	44
Figure 2.12 Typical band forms for secondary amides in 1600 cm ⁻¹ region.....	44
Figure 2.13 Scheme of reaction system for synthesis of Hg(II)-MMEA complex monomer.....	45
Figure 2.14 Synthesis of Hg(II)-MMEA complex monomer.....	46
Figure 2.15 Conversion of cysteamine to zwitterions form in aqueous solutions.....	46
Figure 2.16 Creating the anionic forms in basic solution.....	46
Figure 2.17 Spectrophotometric titration curves of Cysteamine.....	47
Figure 2.18 Dimerization arising from formation of disulfide bond in presence of oxygen.....	47
Figure 2.19 Scheme of polymerization vessel.....	49
Figure 2.20 Scheme of removing the Hg(II) in acidic thiourea solution.....	50
Figure 2.21 Copolymerization of Hg(II)-N-methacryloyl-2-mercaptoethyl amine complex monomer with EDMA and MAA as cross-linker and functional monomer respectively.....	51
Figure 2.22 Removing the Hg(II) from copolymer in acidic thiourea solution.....	52
Figure 3.1 Binding of a substrate (S) to a molecularly imprinted polymer (MIP).....	55
Figure 3.2 General method of batch rebinding.....	55
Figure 3.3 Adsorption capacity of Hg(II) ions on the imprinted polymer.....	60
Figure 3.4 Effects of pH on Hg(II) adsorption	61
Figure 3.5 Adsorption rates of Hg(II) ions on the imprinted polymer.....	62
Figure 5.1 Steps of producing the polymeric fiber.....	70
Figure 5.2 The capillary tube filled with prepolymer solution and sealed by silicon rubbers.....	71
Figure 5.3 Photograph of the produced polymeric fiber.....	71
Figure 5.4 Thermogravimetry curves of Hg(II)-MMEA complex monomer and Hg(II)-imprinted polymer.....	72
Figure A.1 FTIR spectrum of 2-Mercaptoethyl amine.....	93
Fig. A.2 FTIR spectrum of N-Methacryloyl 2-mecapto ethylamine.....	94
Figure A.3 FTIR spectrum of Hg(II)-N-methacryloyl-2-mercaptoethyl amine complex monomer.....	95
Figure A.4 FTIR spectrum of Methacrylic acid.....	96
Figure A.5 FTIR spectrum of Hg(II)-[(MAA-MMEA)-EDMA] copolymer (unleached).....	97
Figure A.6 FTIR spectrum of Hg(II)-imprinted copolymer (leached).....	98

List of Figures

Figure A.7 IR spectrum of CH ₃ Hg- N-methacryloyl-2-mercaptoethyl amine complex.....	99
Figure A.8 Raman spectrum of Hg(II)-MMEA Complex.....	100
Figure A.9 Raman spectrum of unleached Hg(II)-imprinted copolymer.....	100
Figure A.10 Raman spectrum of leached Hg(II)-imprinted copolymer.....	100

List of Tables

Table 1.1 Free radical initiators with decomposition temperature ranges used to molecular imprinting.....	21
Table 2.1 Outstanding infrared Bands of 2-Mercapto ethylamine.....	43
Table 2.2 Outstanding infrared Bands of N-methacryloyl 2-mercapto ethylamine...	43
Table 2.3 Outstanding infrared Bands of Hg(II)-N-methacryloyl-2-mercapto ethylamine.....	48
Table 2.4 Outstanding infrared Bands of Hg(II)-[(MEA-MAA)-EDMA] Copolymer (unleached).....	53
Table 2.5 Outstanding infrared Bands of Hg(II)-Imprinted Copolymer (leached).....	54
Table 3.1 Adsorption capacities of imprinted polymer in different concentrations of Hg(II).....	60
Table 3.2 Adsorption quantities of Hg ²⁺ in different pHs.....	61
Table 3.3 Adsorption quantities of Hg ²⁺ in different times.....	62
Table 3.4 Initial and final concentration of Hg(II) and competitive ions in binding batch tests.....	63
Table 3.5 The selectivity parameters.....	65
Table 4.1 Determination of Hg(II) in water samples.....	66

Abbreviations

ABDV	Azo N,N'-bis-divaleronitrile
AFS	Atomic Fluorescence Spectrometer
AIBN	2, 2' AzoIsobutyronitrile
DAAB	Diazoaminobenzene
DMSO	Dimethyl Sulfoxide
DVB	Divinyl Benzene
EDMA	Ethylenglycol Dimethacrylate
EGDMA	See EDMA
FTIR	Fourier Transform Infrared Spectrometer
GC	Gas Chromatography
HCl	Hydrochloric acid
HPLC	High-performance Liquid Chromatography
ICP-MS	Inductively Coupled Plasma-Mass Spectrometer
IIP	Ion Imprinted Polymer
kJ/mol	kilo-Joule per mole
MAA	Methacrylic Acid
MEA	2-Mercaptoethyl amine
μg/L	micro gram per liter
mg	milligram
MIP	Molecular Imprinted Polymer
MMEA	N-methacryloyl-2-mercapto ethylamine
ppb	part per billion
ppm	part per million
PVP	Poly Vinyl Pyridine

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